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DETERMINATION OF PCB-CONGENERS IN SEDIMENT SAMPLES USING A RETENTION INDEX SYSTEM

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Summary

A method for the determination of PCB congeners in sediment and particulate matter in described. For identification of the peaks in the gas chromatogram a retention index system was used based on n-alkyltrichloroacetates (ACTAs). The retention index system could also applied if the GC column temperature was programmed.

1. INTRODUCTION

For the determination of PCBs in sediment and particulate matter samples a method had to be developed that includes the determination of the individual congeners by capillary GC-ECD. Especially attention had to be given to the determination of the so-called indicator congeners: 2,4,4'-trichlorobiphenyl, 2,2',5,5'-tetrachlorobiphenyl, 2,2',4,5,5'-pentachlorobiphenyl, 2,2',3,4,4',5'-hexachlorobiphenyl, 2,2',4,4',5,5'-hexachlorobiphenyl and 2,2',3,3,4',5,5'-heptachlorobiphenyl with the corresponding IUPAC numbers 28, 52, 101, 138, 153 and 180. Lateron in the Netherlands also 2,3',4,4',5-pentachlorobiphenyl (118) was selected as indicator biphenyl. These seven compounds give a good impression about the contamination with PCBs, their contribution to the total amount of PCBs is about 10-25%. Identification of the congeners is based on correct retention time. For a correct interpretation of the capillary gas chromatogram with a large amount of PCBs and other peaks use of a retention index system will give more reliable results.

In 1958 Kovats (1) introduced the use of n-alkanes for calculation of GC retention indices. The precision and reproducability of these indices led to general use of these indices especially in the identification of complex mixtures. However this system cannot be applied in combination with detectors e.g. ECD, which are insensitive for alkanes. Neu (2) and Ballschmiter (3) used a series of homologous n-alkyl trichloroacetates (ATCAs). Pacholec and Poole (4) used a series of homologous n-monobromo-alkanes.

Neu compared a couple of homologous series of α-w-dichloro-n-alkanes, α-chloro-n-alkanes, α-bromo-n-alkanes, chlorophenylalkyl ether and ATCAs. The best results were obtained with ATCAs. In this paper the use of ATCAs for the determination of PCB congeners in sediment and particulate matter samples is described.

2. PROCEDURE

2.1. Reagents

For extraction purposes acetone ("Zur Analyse", Merck Darmstadt, FRG) and petroleum ether, distilled (boiling range 40-60°C, Ph.Ned.Brocacef, Maarssen, The Netherlands) were used. Na_2SO_4 (Analar, BDH Chemicals Ltd, Poole, U.K.) was heated at 500°C for 3 h before use. NaCl ("Zur Analyse", Merck), saturated solution in water. For removal of elemental sulfur Na_2SO_3 ("Zur Analyse", Merck), saturated solution in water, was used.

For clean-up basic alumina (W-200, activity Super I, Woelm, Eschwege, FRG) activated before use for 16 h at 150°C next deactivated with 11% w/w water, silica gel (Merck, Kieselgel No 7754, 70-230 mesh) activated 15 h at 200°C before use and quartz wool, extracted 8 h with a mixture of petroleum ether and acetone (4 + 1, v/v).

The individual PCB congeners were obtained from Foxboros Analabs (North Haven, CT, USA) and Promochem G.mb.H. (Wesel, FRG), the technical PCB mixtures Arclor 1232 and Aroclor 1254 from Chrompack Nederland B.V. (Middelburg, The Netherlands).

The ATCAs were not for sale so they had to be synthezised. The synthesis and purification were as follows. 0.04 Mol of an alcohol were dissolved in 50 ml of toluene, 0.04 mol of pyridine and 0.045 mol trichloroacetyl chloride were added and the mixture was heated on a waterbath for about 2 h. After cooling the mixture was transferred into a separation funnel containing 25 ml of a 4% (w/w) solution of $NaHCO_3$. The mixture was gently mixed, the water phase decanted and the toluene phase was washed several times with 25 ml of a 4% (w/w) solution of $NaHCO_3$ till pH 7 was reached. The toluene was dried over anh. Na_2SO_4 and removed by distillation. After cooling 5 ml of petroleum ether were added to the residue and this was brought on a column (40 x 2.0 cm) filled with 75 g of neutral alumina. The column was eluted with 150 ml of petroleum ether. The petroleum ether was removed by distillation.

The ATCAs used for identification were n-octyltrichloroacetate, n-decyltrichloroacetate, n-dodecyltrichloroacetate, n-tetradecyltrichloroacetate, n-hexadecyltrichloroacetate, n-octadecyltrichloroacetate and n-eicocyltrichloroacetate. Octanol, undecanol and pyridine were obtained from Baker, Deventer, The Netherlands, nonanol from BDH, octadecanol and tetradecanol from Aldrich, Brussel, Belgium, pentadecanol, nonadecanol, $NaHCO_3$ and toluene from Merck, decanol, dodecanol, tridecanol, hexadecanol, heptadecanol, eicosanol and trichloroacetylchloride from Fluka, Buchs, Switzerland.

2.2. Extraction

In a centrifuge tube with screw cap 5 ml of water were added to 25 g of sediment or particulate matter. The mixture was shaken with 40 ml of acetone for 20 min. by means of a mechanical shaker. The tube was centrifuged for 10 min. and the acetone phase was decanted into a 1 l separation funnel. The sample in the tube was shaken again with 40 ml of acetone for 20 min. After centrifugation for 10 min. the acetone phase was decanted. To the combined acetone extracts 100 ml of water and 5 ml of a saturated solution of Na_2SO_3 were added next the solution was shaken for 1 min. Next 700 ml of water and 5 ml of a saturated solution of NaCl were added. The solution was shaken 2 times with 50 ml of petroleum ether for 20 min. by a mechanical shaker. The petroleum ether phases were decanted and the combined petroleum ether extracts were dried over anh. Na_2SO_4 and concentrated in a Kuderna-Danish apparatus to about 5 ml. The extract was brought in a volumetric flask of 25 ml and filled up with petroleum ether.

2.3. Clean-up

One ml of the extract was added to a column (23 x 0.6 cm I.D.) containing a plug of quartz wool and 2.0 g of basic alumina. For rinsing 3 portions of 0.5 ml of petroleum ether were used. The column was eluted with 10 ml of petroleum ether to produce Eluate A. The eluate was concentrated to 1 ml by a gentle stream of nitrogen at room temperature. The concentrated eluate was added to a column (40 x 0.9 cm I.D.) containing a plug of quartz wool, 0.5 g of anh. Na_2SO_4, 5.0 g silicagel and 0.5 g of anh. Na_2SO_4. For rinsing 3 portions of 0.5 ml of petroleum ether were used. The column was eluted with 46 ml of petroleum ether to produce Eluate C, containing HCB, heptachlor, aldrin, isodrin, p.p'-DDE, o.p'-DDT, p.p'-DDT (60%) and PCBs. The eluate was concentrated to 1 ml by a gentle stream of nitrogen at room temperature.

2.4. GC

One µl of the concentrated eluate was injected into a Hewlett Packard Model 5880 GC-^{63}Ni ECD. Instrument parameters and operational conditions were as follows: separation column: fused silica WCOT (50 m x 0.33 mm I.D., Chrompack; stationary phase: CP Sil 5, film thickness 0.15 µm; temperatures: oven isothermal at 80°C for 3 min, next programmed 80-270°C at 2.5°C min^{-1}; injection block 200°C; detector 300°C; carrier gas helium 111.5 kPa, constant pressure; purge gas argon +10% methane, flowrate 40 ml min^{-1}; splitless injection; automatic liquid sampler; electronic integrator level four with data storage on a cartridge tape unit and BASIC programming for data processing.

2.5. Recovery and detection limit

Sediment samples were spiked with Aroclor 1232 and Aroclor 1254. Seven days after spiking the samples were extracted. The mean recovery ± rel. S.D. was 84 ± 9%. The detection limit was 0.002-0.005 mg kg^{-1} on a dry weight base (sediment sample was dried for 4 h at 105°C).

2.6. Calculation retention indices

In literature use of n-alkane is described for calculation of retention indices also if a temperature program was used during the GC analysis (5). In this paper the use of ATCAs in combination with a GC temperature program is described. In Fig.1 the calculation formula is given. After data storage of chromatographic runs from injections of ATCA reference standards, PCB congeners standards and samples collected for a period of 24 h the following calculations were made with the integrator of the GC by means of a computer program in basic:

- PCB reference standard: the mean and standard deviation of the retention index for each PCB congener and a retention index window equal to mean ± 3 times the standard deviation of the retention index
- samples: the retention index and the amount of the PCB congener and a remark if the retention index of the PCB congener is outside the window.

3. RESULTS

In Fig.2 retention time (RT) versus alkyl chain length are given for n-alkanes and ATCAs with a same column temperature program. In Fig.3 GC separation of ATCAs and PCBs are given. In Table I the reproducability of RT of ATCA at different time intervals are summarized. The results are obtained with the same chromatographic column and with the same GC.

For PCB congeners the mean standard deviation is 0.29 retention index units (0.62 s retention time) in the area 1400-1600 retention index units. The GC peak width at half peak height is 6 s (2.8 retention index units) which means that the resolving power of the ATCA index system is enough.

The ATCA index system is used during the analysis of PCB congeners in sediment and particulate matter samples for a monitoring program of surface water of the Netherlands. In Table 2 the retention indices of 6 PCB congeners determined in sediment samples are summarized. From these results it follows that the retention index of peak 52 is out of the 3 S.D. limit. In Table 3 as an example the sum of 5 PCB congeners for a couple of sampling sites are given (28, 101, 138, 153 and 180).

4. CONCLUSION

Use of ATCA as external retention standard for determination of retention indices at temperature programmed gas chromatography gives an adequate resolution for identification of peaks in complex PCB mixtures.

5. REFERENCES

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Figure 1

CALCULATION OF RETENTION INDEX (I) AND TEMPERATURE PROGRAMMED GLC

FORMULA:

$$I(X)=I(1)+[I(2)-I(1)]\,[t(X)-t(1)]\,/\,[t(2)-t(1)]$$

I(X)=RET.INDEX OF PCB COMPONENT
I(1),I(2)=RET.INDEX OF ATCA(1) AND (2)
t(X)=RET.TIME OF PCB COMPONENT
t(1),t(2)=RET.TIME OF ATCA (1) AND (2)

PREDICTIONS:

- ***INITIAL TEMP. LOW ENOUGH TO IMMOBILIZE THE SOLUTE***
- ***I(ATCA)=100X (C NUMBER ALKYL GROUP)***
- ***A LINEAR RELATIONSHIP BETWEEN I AND t.***

(IN FACT THE RELATIONSHIP IS NOT PURELY LINEAR. WHEN USING ATCAs WITH A DIFFERENCE IN C NUMBER OF 1 THE ERROR WILL BE SMALL).

Figure 2

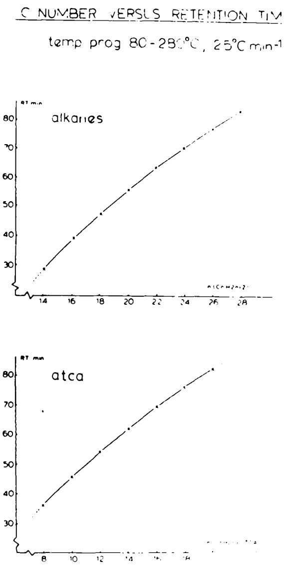

Figure 3

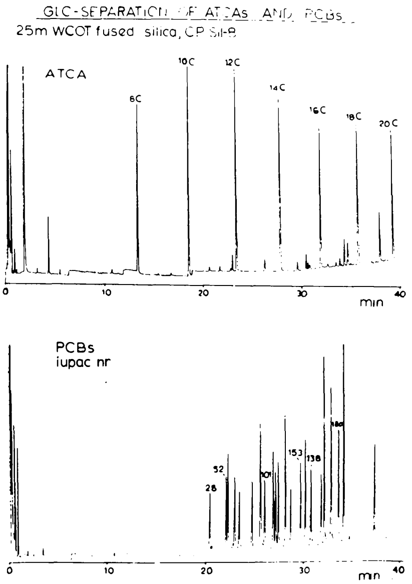

Table 1

REPRODUCIBILITY OF RT OF ATCA
$\bar{X}$ AND RELATIVE S.D., N=2
AT DIFFERENT TIME INTERVALS
(ΔI= S.D. OF RET.INDEX I)

ATCA	TIME INTERVAL	
	3h	24h
C8 I=800	30.889±0.0125 ΔI=0.32	30.919±0.0472 ΔI=1.22
C10 I=1000	40.161±0.0142 ΔI=0.35	40.182±0.0507 ΔI=1.26
C12 I=1200	48.689±0.0160 ΔI=0.39	48.709±0.0507 ΔI=1.25
C14 I=1400	56.499±0.0178 ΔI=0.44	56.518±0.0516 ΔI=1.28
C16 I=1600	63.683±0.0214 ΔI=0.54	63.701±0.0534 ΔI=1.34
C18 I=1800	70.310±0.0276 ΔI=0.71	70.330±0.0632 ΔI=1.62
C20 I=2000	76.457±0.0258 ΔI=0.67	76.477±0.0623 ΔI=1.63

RET.INDICES OF PCBs IN SEDIMENT

Table 2

IUPAC NUMBER	STANDARD(n=4) $\bar{X}$ S.D.	3. S.D.LIMIT	SAMPLING SITE		
			1.RHINE RIVER AT LOBITH	4.WAAL RIVER AT TIEL	12.NIEUWE MAAS R.
28	1077.77±0.420	1076.51–1079.03	1077.16	1077.72	1078.17
52	1143.70±0.442	1142.38–1145.02	1145.04	1145.51	1146.05
101	1313.82±0.459	1312.44–1315.20	1313.37	1313.88	1314.49
138	1536.12±0.419	1534.86–1537.38	1535.77	1536.24	1536.96
153	1485.24±0.465	1483.85-1486.64	1484.68	1485.21	1485.96
180	1683.06±0.475	1681.84–1684.49	1682.65	1683.10	1684.09

SUM OF CONCENTRATIONS OF SIX INDIVIDUAL PCBs IN SEDIMENT

Table 3

SAMPLING SITE:	CONCENTRATION (mg/kg ON DRY WEIGHT BASIS)
1.RHINE RIVER AT LOBITH	••••••••••••••••••••••••••••••••(0.32)
12.NIEUWE MAAS R. AT ROTTERDAM	••••••••••••••(0.14)
14.MAAS AT EYSDEN	•••••••••••••••••(0.17)
16.MAAS AT VENLO	••••••••••(0.10)
8.BIESBOSCH AT SPIJKERBOOR	•••••••••••••••(0.15)
28.IJSSEL RIVER AT KAMPEN	••••••(0.06)
26.IJSSEL LAKE AT MUNNIKPLAAT	•(<0.01)
20.WESTERSCHELDE AT VLISSINGEN	•(<0.01)
31.WADDEN SEA	•(<0.01)